ICP-OES measurement of some transition metals in HF acid media

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Publication date:
2017

Document Version
Publisher's PDF, also known as Version of record

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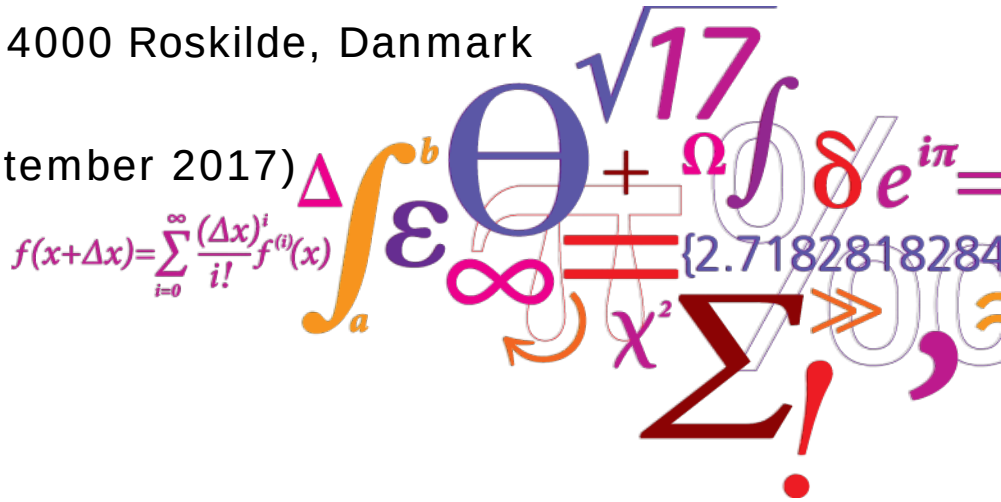
NKS-B ICP User Seminar (25-27 September 2017)



DTU Nutech
Center for Nukleare Teknologier

Introduction 1

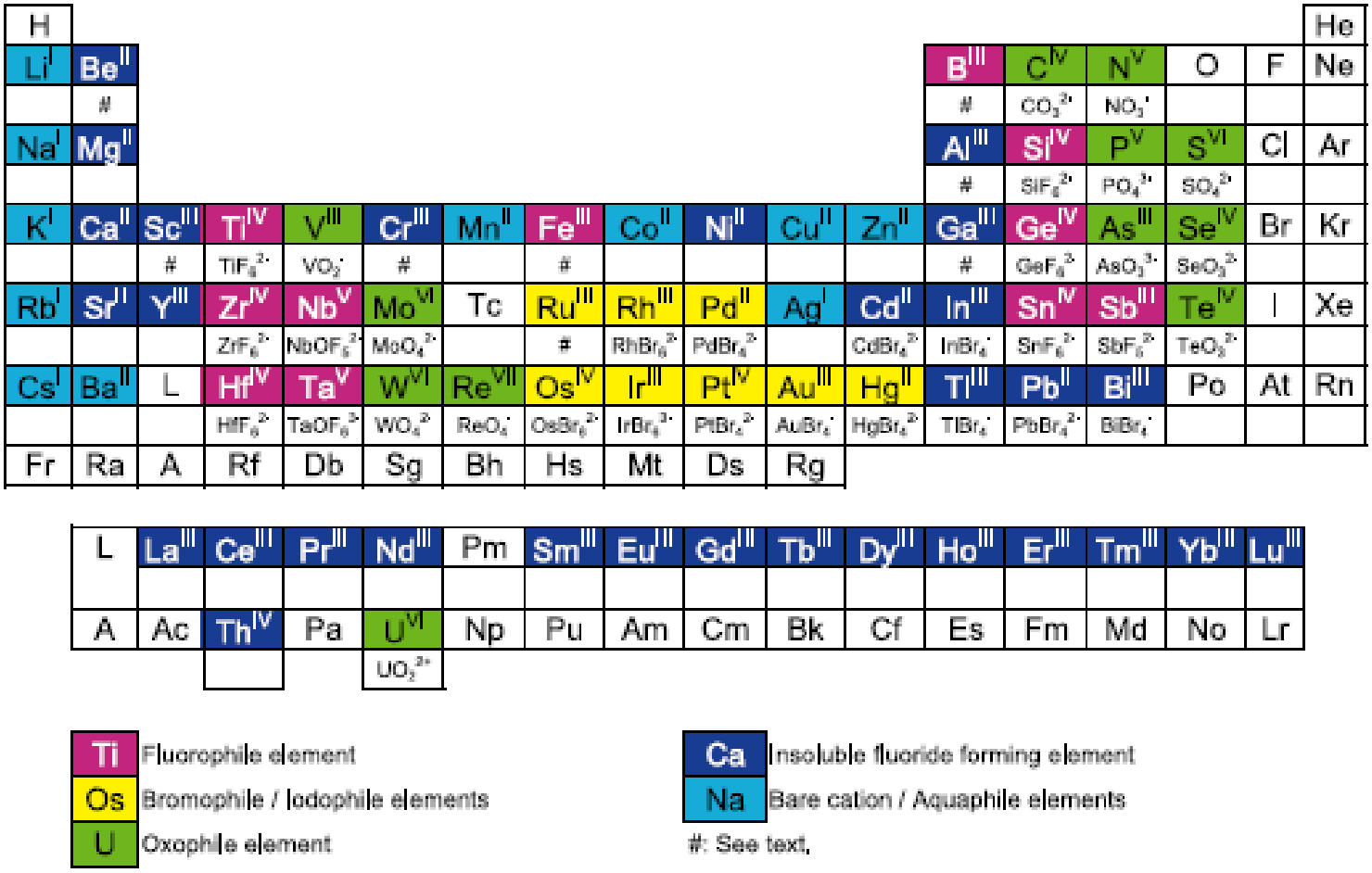
- Method has to be developed for determination of ^{93}Mo, ^{94}Nb (and ^{93}Zr) from nuclear power plant wastes (for example steel samples).
- Many preliminary experiments for method developement have to be performed: a relatively fast and easy technique is needed to understand the chemical behavior of Mo and Nb (and Zr).

- Easy-to-measure isotopes (gamma-emitters): ^{95}Zr → ^{95}Nb
  - ^{95}Zr ($t_{1/2}$ = 64 days): 724 keV (44%) and 756 keV (54%) gamma-line
  - ^{95}Nb ($t_{1/2}$ = 35 days) : 765 keV (100%) gamma-line
  - No such isotope of Mo exists.
- No more working nuclear reactors at Risø! Without it the named radionuclides are very expensive to have (purchase).

- We have to rely on the stable isotopes of natural composition of these analytes. Their concentrations are measured using ICP-OES.

- Zr and Nb are „flourofil” elements. [Anal Sci 25 (2009) 1181-1187]

„Fluorophil" elements



Introduction 2

- ^{94}Nb can be measured by gamma-spectrometry.
  - Radionuclides causing the Compton continuum have to be removed.
- ^{93}Mo can be measured by ICP-MS, LSC or X-ray spectrometry.
  - Each detection type needs a very pure source.
- A very effective method is needed. (Probably a several-steps method)
- Effectivity of each step has to be determined.
  - Decontamination factor (DF), separation factor

$$DF_{component} = A_{component,\ before\ separation\ (step)} / A_{component,\ after\ separation\ (step)}$$

$$DF_{component} = m_{component,\ before\ separation\ (step)} / m_{component,\ after\ separation\ (step)}$$

- To avoid the contamination of our laboratory, most preliminary experiments are performed using stable nuclides and ICP-OES as detection technique.

Equipment 1

Equipment 2

- Hardware: Varian Vista AX CCD Simultaneous ICP-AES
- Software: ICP Expert II (Agilent Vista PRO Instrument Software, version 2.0)

- Ca. 3 mL sample is needed (1 M alkali ... 1 M acid)
- Blank: 3% HNO_3

- The main difficulty:
  - HF acid is practically always needed when dissolving and separating Nb and Zr, so it is present in all of the samples to be measured.
  - However, HF damages the glassware of the ICP-OES equipment.

$$SiO_2 + 4\ HF \rightarrow SiF_4 + 2\ H_2O$$

- How to avoid this damage?
  - Dilution
  - Evaporation
  - Complexation

Dilution

- Authors of some papers (for example: Prog Nucl En 93 (2016) 362-370) do not take care of presence of F^- when its concentration is below 0.005 M.

- So dilution might be used in certain cases.
  - Typically when HF concentration is not much higher than the given level (for example: 0.01 M or 0.02 M).

- But dilution also decreases the concentration of the analytes, so it cannot be widely used.
  - ”Official” limits of detection: Mo: 4 ppb = µg/L = ng/mL
    Nb: 4 ppb
    Zr: 1.5 ppb

Evaporation

- Avoiding HF is practically impossible, as Zr and Nb can practically not be (and do not remain) dissolved without F^-. (Remember, they are “fluorophile” elements.)
- But the concentration of F^- can be decreased significantly.

- For example: in case of 10 mL ≥1 M HF (for example 2 M, 4 M, 6 M etc.)
  - evaporation
  - taking up in 100 µL cc. HF + 100 µl cc. HNO_3
  - dilution to 10 mL
  - Result: 0.28 M HF / 0.16 M HNO_3

- Don´t forget to protect the glass window of your fume hood!

Complexation

- For complexation of excess F^-, boric acid can be used (J Anal At Spectrom 11 (1996) 287-296):

$$4\ HF + H_3BO_3 \rightarrow HBF_4 + 3\ H_2O$$

- It has to be taken into account, that boric acid increases the number of false signals:
  - Mo: 201.512 nm line
  - Zr: 343.823 nm line
  - Fe: 234.830, 273.358 and 373.713 nm lines
  - Ni: 230.299 nm line
  - Mn: 344.199 nm line

Further difficulties 1

- ”Real time” analysis is not possible; results are produced some days after the experiment.
  - Correction of experiment´s parameters is mainly not possible.
  - A huge drawback compared to gamma-spectrometry.

- (But measurement of an individual sample is much faster.)

Further difficulties 2

- A very wide range of concentrations has to be managed.
  - Composition of NIST Standard Reference Material 123c Stainless Steel (AISI 348) - a test material:

    mainly (68.52%) Fe,
    17.40% Cr,
    11.34% Ni,
    1.75% Mn,
    0.65% Nb,
    0.22% Mo,
    0.12% Co.
  - Fe/Mo ≈ 311
  - If Mo ≈ 4 ppb (LOD) => Fe ≈ 1400 ppb
  - If Mo ≈ 100 ppb => Fe ≈ 30000 ppb

- Samples can be diluted; but isolation or separation are not possible, as we want to characterize the separation steps!

Further difficulties 3

- Many other false signals arise, such as (for example):
  - Mo: 281.615 nm line — Al, Mn
    284.824 line — Nb
  - Nb: 210.942 nm line — Fe, Mn
    309.417 nm line — Cr, Mo
  - Zr: 256.889 nm line — Fe
    343.823 nm line — Nb
  - Fe: 234.350 nm line — Cr
    258.588 nm line — Mo
    261.382 nm line — Cr
  - Cr: 286.674 nm line — Mo
  - Ni: 227.021 nm line — Cr
    230.078 nm line — Nb
  - Mn: 261.815 nm line — Fe, Cr

Measurement of Mo by ICP-OES [ppb]

Tube	Sample Labels	Mo 201,512	Mo 202,032	Mo 203,846	Mo 204.598	Mo 281.615	Mo avg.	Mo std(s)																Real
1	Blank	0	0	0	0	0	0,0	0,0																
2	Standard 1	153	153	153	153	153	153,0	0,0																
3	Standard 2	765	765	765	765	765	765,0	0,0																
4	Standard 3	1530	1530	1530	1530	1530	1530,0	0,0																
5	Water	4,6777	9,04198	3,2856	3,44991	6,90859	5,5	2,5																
6	0,01/Std-3 1,5x	328,518	325	321,406	336,727	330,724	328,5	5,8		329	325	321	337	331	328									**330**
7	0,01/Std-3 +FeMnSr	217,545	270,03	342,122	283,395	682,736	359,2	186,2		218	270	342	283	683	359		-41%	-18%	6%	-17%	69%	9%		
8	0,01/Std-4 1,5x	675,89	669,122	670,966	680,944	660,39	671,5	7,7		676	669	671	681	660	671									**660**
9	0,01/Std-4 +FeMnSr	487,366	527,268	625,329	562,79	969,818	634,5	194,2		487	527	625	563	970	635		-32%	-24%	-7%	-19%	38%	-6%		
10	0,01/Std-5	1475	1519,79	1503,04	1501,32	1491,37	1498,1	16,5		1475	1520	1503	1501	1491	1498									**1485**
11	0,01/Std-5 +FeMnSr	893,052	913,341	1008,56	960,142	1267,81	1008,6	151,6		1161	1187	1311	1248	1648	1311		-24%	-25%	-14%	-18%	10%	-13%		
12	Water	5,40442	12,2196	5,68364	8,37302	7,36536	7,8	2,8																
13	0,50/S-3 1,5x	212,828	224,554	218,983	228,889	220,619	221,2	6,0		213	225	219	229	221	221									**222**
14	0,50/S-3 +FeMnSr	151,809	179,594	255,309	196,227	647,501	286,1	205,6		152	180	255	196	648	286		-33%	-22%	15%	-15%	98%	26%		
15	0,50/S-4 1,5x	435,827	441,378	438,954	444,3	438,808	439,9	3,2		436	441	439	444	439	440									**444**
16	0,50/S-4 +FeMnSr	307,817	348,675	428,102	358,454	757,646	440,1	182,7		308	349	428	358	758	440		-34%	-23%	-3%	-21%	53%	0%		
17	0,50/S-5	980,796	967,37	961,872	983,639	972,237	973,2	9,1		981	967	962	984	972	973									**1000**
18	0,50/S-5 +FeMnSr	526,26	578,333	679,08	615,579	1071,15	694,1	218,0		684	752	883	800	1392	902		-36%	-25%	-9%	-21%	36%	-8%		
19	Water	-4,46468	9,0319	9,62996	9,69169	7,84647	7,2	4,1																

Measurement of Nb by ICP-OES [ppb]

Tube	Sample Labels	Nb 210.942	Nb 269.706	Nb 295.088	Nb 309.417	Nb 313.078	Nb avg.	Nb std(s)															Real
1	Blank	0	0	0	0	0	0,0	0,0															
2	Standard 1	66	66	66	66	66	66,0	0,0															
3	Standard 2	330	330	330	330	330	330,0	0,0															
4	Standard 3	660	660	660	660	660	660,0	0,0															
5	Water	-1,08373	7,84935	6,0011	7,38264	4,9313	5,2	3,1															
6	0,01/Std-3 1,5x	347,141	350,776	344,227	345,668	340,226	345,6	3,9		347	351	344	346	340	346								**330**
7	0,01/Std-3 +FeMnSr	803,626	342,184	283,395	263,052	279,061	394,3	230,8		804	342	283	263	279	394		79%	-2%	-19%	-27%	-20%	13%	
8	0,01/Std-4 1,5x	708,465	703,504	700,156	703,598	695,564	702,3	4,8		708	704	700	704	696	702								**660**
9	0,01/Std-4 +FeMnSr	#NAME?	611,685	583,453	556,116	572,731	581,0	23,3			612	583	556	573	581			-14%	-18%	-23%	-19%	-19%	
10	0,01/Std-5	-4,26196	3,15501	3,74386	6,9297	4,46885	3,7	2,5		-4	3	4	7	4	4								**0**
11	0,01/Std-5 +FeMnSr	622,167	71,6067	80,1575	5,72571	3,69986	156,7	262,7		809	93	104	7	5	204								
12	Water	-8,15695	1,89255	4,54518	6,50673	4,64806	3,5	2,6															
13	0,50/S-3 1,5x	235,654	226,956	226,122	219,323	220,362	225,7	6,5		236	227	226	219	220	226								**222**
14	0,50/S-3 +FeMnSr	722,795	228,197	192,758	164,957	190,313	299,8	237,5		723	228	193	165	190	300		102%	1%	-16%	-28%	-15%	28%	
15	0,50/S-4 1,5x	455,704	462,436	453,073	452,21	449,807	454,6	4,8		456	462	453	452	450	455								**444**
16	0,50/S-4 +FeMnSr	881,687	408,003	373,809	353,293	369,1	477,2	227,0		882	408	374	353	369	477		64%	-13%	-19%	-25%	-20%	5%	
17	0,50/S-5	-0,875903	0,437722	9,2251	6,33497	10,0194	5,2	4,8		-1	0	9	6	10	5								**0**
18	0,50/S-5 +FeMnSr	607,103	67,6454	87,7876	7,08947	4,80899	154,9	255,4		789	88	114	9	6	201								
19	Water	8,20094	4,67413	3,29971	6,94485	4,97507	5,6	1,9															

Conclusions

- ICP technique can be used for development of a radioanalytical method (determination of recoveries of analytes and decontamination factors of disturbing components); but some strange or unusual difficulties can arise.

Thank you very much

for this challenging task, and
for your kind attention.